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# THE EFFECT OF SULPHANILAMIDE ON THE ELECTRODEPOSITION OF COPPER ONTO A SINGLE-CRYSTAL Cu(100) PLANE AND A POLYCRYSTALLINE COPPER SUBSTRATE

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## Summary

Studies were made of the electrodeposition of copper onto a single-crystal Cu(100) plane and onto a polycrystalline copper surface both in pure acidic copper sulphate solution and in solutions containing various concentrations of sulphanilamide at various current densities. On the (100) plane at lower current densities there is a transition from layers to ridges and then to polycrystalline growth with increasing sulphanilamide concentration but at higher current densities the transition is from pyramids to truncated blocks to ridges and then to a polycrystalline deposit. On a polycrystalline substrate there is a change from large grains to very fine grains in the presence of sulphanilamide. These changes are explained with the help of complexation and adsorption theory.

## 1. Introduction

It is known [1, 2] that the epitaxial growth of copper depends largely on the orientation of the substrate and the bath conditions. Furthermore, it has been shown that in purified solutions characteristic growth occurs when copper is deposited onto oriented copper surfaces [3, 4] and that habit modification takes place when the deposition conditions are altered [3 - 6].

Addition agents are used in plating baths to increase the brightness, the smoothness etc. It is known that the presence of sulphur compounds [7 - 9] affects the nature of the electrodeposits and the electrochemical parameters. It has also been observed by the authors that on the (110) plane [10] at very low concentrations of sulphanilamide there is a remarkable change in the electrodeposits. In the present paper we report the effect of sulphanilamide on the electrochemical parameters and morphology of copper electrodeposits.

## 2. Experimental

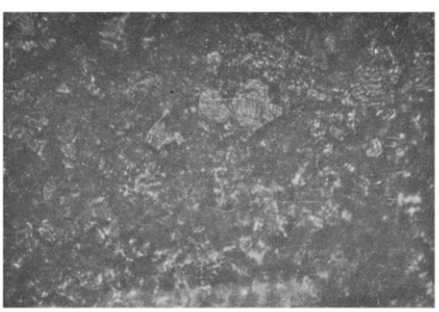
The experimental procedure has been described in detail elsewhere [11] A (100) face of a copper single crystal (checked by X-ray diffraction) was first mechanically polished on 3/0 and 4/0 emery paper using ethyl alcohol as lubricant and was then electropolished [12] in 50% orthophosphoric acid at a constant cell potential of 1.2 V. After electropolishing, the crystal was washed with 10% orthophosphoric acid and triply distilled water and was transferred immediately to the electrolytic cell. The electrolytic bath was a highly purified solution of 0.25 M $CuSO_4$ and 0.1 M $H_2SO_4$. A known amount of sulphanilamide was added to the bath as required and the deposition was carried out at 2, 5, 10 and 15 mA cm $^{2}$ to a thickness corresponding to 3.6 μm with a coulombic charge of 10 C cm $^{2}$. The cathodic overpotential was measured with reference to a freshly prepared copper electrode to an accuracy of ±5 mV using an Elico digital pH meter. The surface morphology of the deposits was examined under a phase contrast microscope at a magnification of 625× and microphotographs were taken. A similar procedure was adopted for the deposition of copper onto a polycrystalline copper surface.

## 3. Results

### *3 1. Surface morphology*

#### *3.1.1. On a polycrystalline surface*

When copper was deposited from pure solution onto a polycrystalline copper surface at 10 mA $cm^{-2}$ the deposit consisted of large grains (Fig. 1). The size of the grains was smaller (Fig. 2) when the bath contained $10^{-9}$ mol $l^{-1}$ sulphanilamide and on increasing the concentration of sulphanilamide to $10^{-5}$ mol $l^{-1}$ a very fine-grained deposit was obtained (Fig. 3). At very high concentrations of sulphanilamide the surface was highly corroded and there was pitting. The deposit appeared dark reddish brown and non-uniform. Similar results were observed at 2, 5 and 15 mA cm $^{2}$.



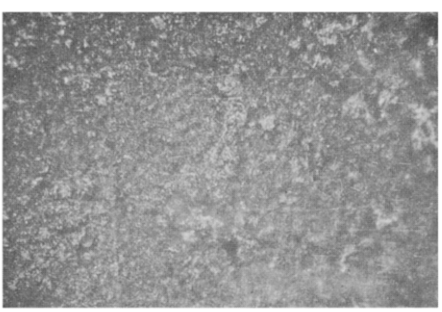
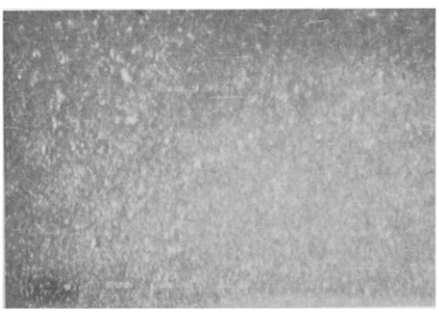


Fig 1. Copper deposited onto a polycrystalline copper substrate from a pure acidic copper sulphate bath at 10 mA $cm^{-2}$. (Magnification, 500× )

Fig 2 Deposit grown on a polycrystalline copper substrate in the presence of $10^{-9}$ mol $l^{-1}$ sulphanilamide at 10 mA $cm^{-2}$ (Magnification, 500× )

*3.1.2. On the (100) plane*

*3.1.2.1. At 2 mA cm $^{-2}$.* When copper was deposited from pure solution onto Cu(100) a layer type of growth was observed in earlier work [14] (*cf.* Fig. 7). When the concentration of sulphanilamide was $10^{-11}$ mol $l^{-1}$ large blocks were observed (Fig. 4). On increasing the concentration to $10^{-9}$ mol $l^{-1}$ smaller blocks were obtained (Fig. 5). At $10^{-7}$ mol $l^{-1}$ small layers were produced (Fig. 6) and at $10^{-6}$ mol $l^{-1}$ ridge growth was observed (*cf.* Fig. 10). A further increase in the concentration to $10^{-5}$ mol $l^{-1}$ resulted in a polycrystalline deposit.



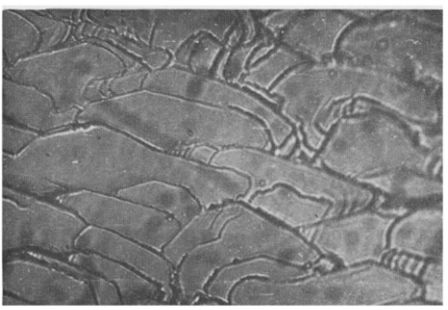
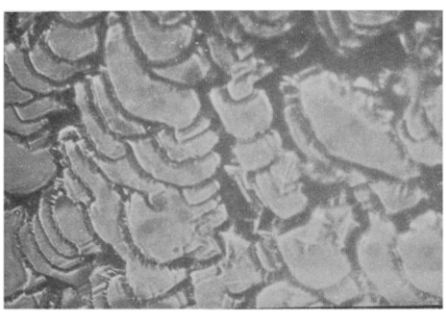


Fig. 3. Deposit grown on a polycrystalline copper substrate in the presence of $10^{-5}$ mol $l^{-1}$ sulphanilamide at 10 mA cm $^{-2}$. (Magnification, 500 × .)

Fig 4. Large blocks deposited onto Cu(100) in the presence of $10^{-11}$ mol $l^{-1}$ sulphanilamide at 2 mA cm $^{-2}$ (Magnification, 500 × )



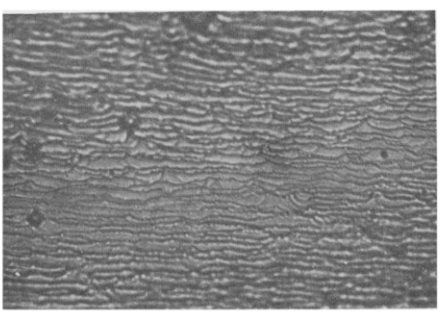
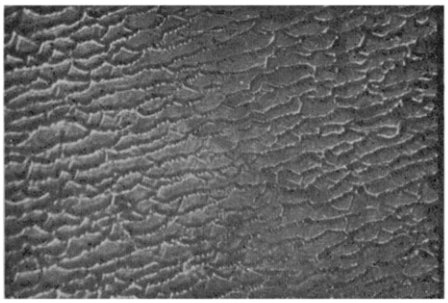


Fig. 5. Smaller blocks (*cf* Fig. 4) deposited onto Cu(100) in the presence of $10^{-9}$ mol $l^{-1}$ sulphanilamide at 2 mA cm $^{-2}$. (Magnification, 500 × )

Fig 6. Small layers deposited onto Cu(100) in the presence of $10^{-7}$ mol $l^{-1}$ sulphanilamide at 2 mA cm $^{-2}$ (Magnification, 500 × )

*3.1.2.2. At 5 mA cm $^{-2}$.* For pure solution, layer growth was observed (Fig. 7). When the concentration of sulphanilamide in the bath was $10^{-11}$ mol $l^{-1}$ a smooth deposit was obtained (Fig. 8) but with an increased concentration of $10^{-9}$ mol $l^{-1}$ the layers started breaking up and at $10^{-8}$ mol $l^{-1}$ completely broken layers were produced (Fig. 9). At $10^{-6}$ mol $l^{-1}$ irregular ridges were observed (Fig. 10). A further increase in the concentration of sulphanilamide to $10^{-5}$ mol $l^{-1}$ resulted in polycrystalline growth.



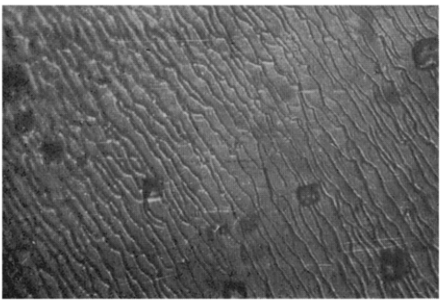
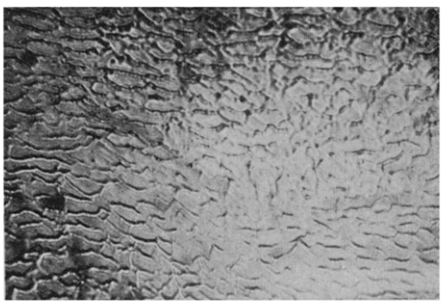


**Fig. 7. Layer growth on Cu(100) from a pure acidic copper sulphate bath at 5 mA $cm^{-2}$ (Magnification, 500 ×.)**

Fig 8 A smooth layer deposited onto Cu(100) in the presence of $10^{-11}$ mol $l^{-1}$ sulphanilamide at 5 mA $cm^{-2}$ (Magnification, 500 ×.)



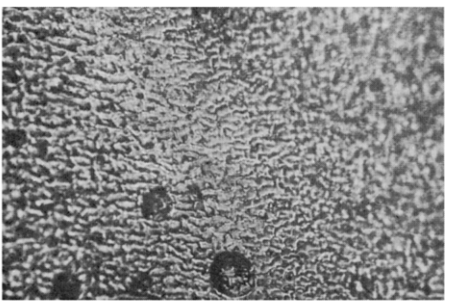
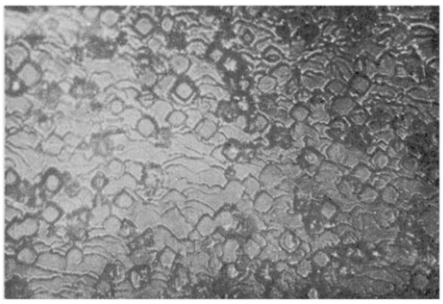


Fig. 9 Broken layers deposited onto Cu(100) in the presence of $10^{-8}$ mol $l^{-1}$ sulphanilamide at 5 mA $cm^{-2}$ (Magnification, 500 ×.)

Fig 10 Irregular ridges deposited onto Cu(100) in the presence of $10^{-6}$ mol $l^{-1}$ sulphanilamide at 5 mA $cm^{-2}$ (Magnification, 500 × )

*3.1.2.3. At 10 mA $cm^{-2}$.* When copper was deposited onto Cu(100) from pure solution at 10 mA $cm^{-2}$ a layer type of growth with pyramids was observed (*cf.* Fig. 15). There was no change in the morphology when $10^{-11}$ mol $l^{-1}$ sulphanilamide was added to the bath. On increasing the concentration to $10^{-10}$ mol $l^{-1}$, truncated pyramids were obtained in a background of layers (Fig. 11). At $10^{-8}$ mol $l^{-1}$ blocks and truncated pyramids were observed (Fig. 12) and at $10^{-7}$ mol $l^{-1}$ dragged blocks and ridges formed (Fig. 13). On increasing the concentration to $10^{-6}$ mol $l^{-1}$ ridge growth was observed (Fig. 14). A further increase in the concentration to $10^{-5}$ mol $l^{-1}$ resulted in polycrystalline growth.

*3.1.2.4. At 15 mA $cm^{-2}$.* When copper was deposited at 15 mA $cm^{-2}$ onto Cu(100) in pure solution a large number of pyramids in a background of layers was observed (Fig. 15). At a concentration of $10^{-10}$ mol $l^{-1}$ sulphanilamide the number of pyramids was less and blocks appeared (Fig. 16). At $10^{-9}$ mol $l^{-1}$ pyramids, truncated pyramids and layers were obtained



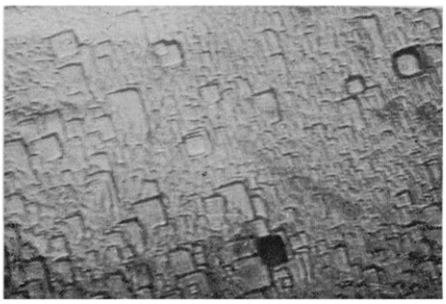


Fig. 11. Truncated pyramids in a background of layers deposited onto Cu(100) in the presence of $10^{-10}$ mol $l^{-1}$ sulphanilamide at 10 mA $cm^{-2}$. (Magnification, 500 ×.)

Fig. 12. Blocks and truncated pyramids deposited onto Cu(100) in the presence of $10^{-8}$ mol $l^{-1}$ sulphanilamide at 10 mA $cm^{-2}$. (Magnification, 500 × )

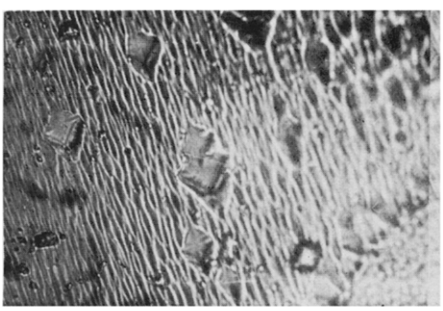
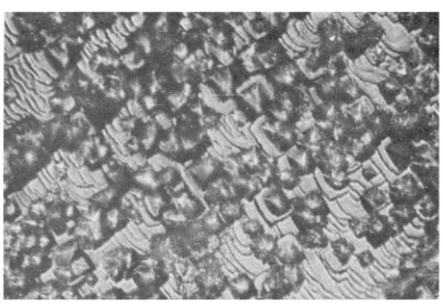


Fig. 13. Dragged blocks and ridges deposited onto Cu(100) in the presence of $10^{-7}$ mol $l^{-1}$ sulphanilamide at 10 mA $cm^{-2}$ (Magnification, 500 ×.)

Fig 14 Ridges deposited onto Cu(100) in the presence of $10^{-6}$ mol $l^{-1}$ sulphanilamide at 10 mA $cm^{-2}$ (Magnification, 500 ×.)



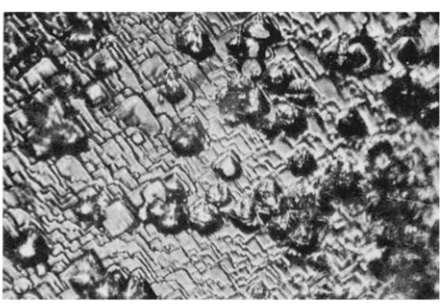
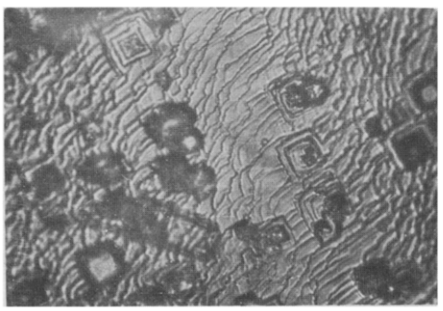


Fig. 15. Pyramids in a background of layers deposited onto Cu(100) from a pure acidic copper sulphate bath at 15 mA $cm^{-2}$ (Magnification, 500 ×.)

Fig. 16. Pyramids in a background of blocks deposited onto Cu(100) in the presence of $10^{-10}$ mol $l^{-1}$ sulphanilamide at 15 mA $cm^{-2}$ (Magnification, 500 ×.)

(Fig. 17). An increase in the concentration to $10^{-8}$ mol $l^{-1}$ produced completely truncated large pyramids (Fig. 18). At $10^{-7}$ mol $l^{-1}$ sulphanilamide occasional truncated blocks were observed in a background of ridges (Fig. 19). With further increase in concentration to $10^{-6}$ mol $l^{-1}$ ridges only were observed (*cf.* Fig. 14). At $10^{-5}$ mol $l^{-1}$ the deposit was polycrystalline with occasional large pyramids (Fig. 20).



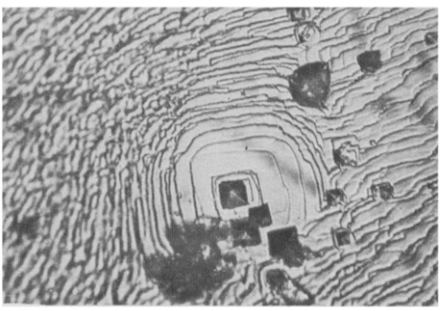
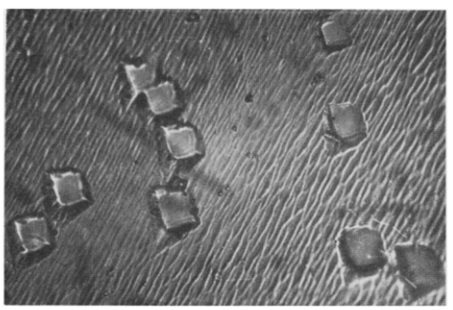


Fig 17 Pyramids, truncated pyramids and layers deposited onto Cu(100) in the presence of $10^{-9}$ mol $l^{-1}$ sulphanilamide at 15 mA $cm^{-2}$ (Magnification, 500×)

Fig 18. Truncated pyramids deposited onto Cu(100) in the presence of $10^{-8}$ mol $l^{-1}$ sulphanilamide at 15 mA $cm^{-2}$ (Magnification, 500×)



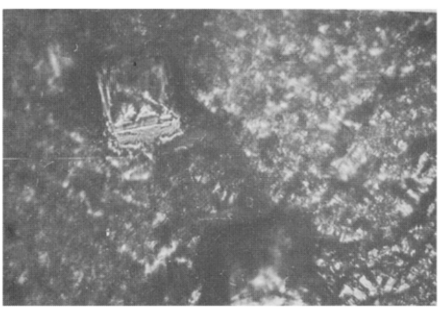


Fig. 19. Truncated blocks in a background of ridges deposited onto Cu(100) in the presence of $10^{-7}$ mol $l^{-1}$ sulphanilamide at 15 mA $cm^{-2}$ (Magnification, 500×)

Fig 20 A polycrystalline deposit with occasional large pyramids deposited onto Cu(100) in the presence of $10^{-6}$ mol $l^{-1}$ sulphanilamide at 15 mA $cm^{-2}$ (Magnification, 500×)

### *3.2. Overpotential*

#### *3.2.1. On a polycrystalline surface*

In pure solution the overpotential initially increased and attained a constant value on the polycrystalline copper surface at all current densities. In the presence of low concentrations of sulphanilamide ($10^{-9}$ - $10^{-5}$ mol $l^{-1}$) the behaviour remained the same. With concentrations of sulphanilamide higher than $10^{-5}$ mol $l^{-1}$ there was no regularity in the variation. The Tafel relation held good only at low concentrations of sulphanilamide ($10^{-9}$ - $10^{-5}$ mol $l^{-1}$) (Fig. 21).

The Tafel slope (Fig. 21) was found to be 126.2 mV in pure solution and the exchange current density was 1.8 mA $cm^{-2}$. However, in the presence of sulphanilamide ($10^{-9}$ - $10^{-5}$ mol $l^{-1}$) the slopes and the exchange current densities were found to be about 132.9 mV and 1.7 - 1.4 mA $cm^{-2}$ respectively.

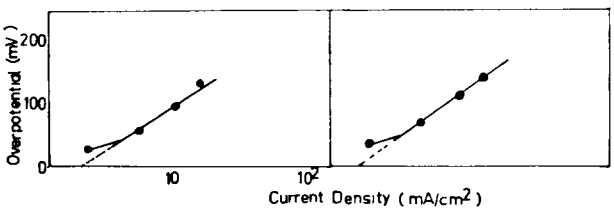



Fig 21 Overpotential *vs* current density for copper deposition onto polycrystalline copper in (a) pure acidic copper sulphate solution and (b) copper sulphate solution containing $10^{-9}$ mol $l^{-1}$ sulphanilamide (a) $i_0$ = 1 8 mA $cm^{-2}$, $b$ = 126 2 mV, (b) $i_0$ = 1 7 mA $cm^{-2}$, $b$ = 132.9 mV

*3.2.2. On the (100) plane*

The overpotential during deposition increased with time and attained a steady value when copper was deposited from a pure acidic copper sulphate bath at all current densities. When the deposition was carried out in the presence of sulphanilamide ($10^{-11}$ - $10^{-5}$ mol $l^{-1}$) the same trend of first an increasing overpotential and then a steady value was observed. The overpotential did not vary with time when ridge growth was observed. Even

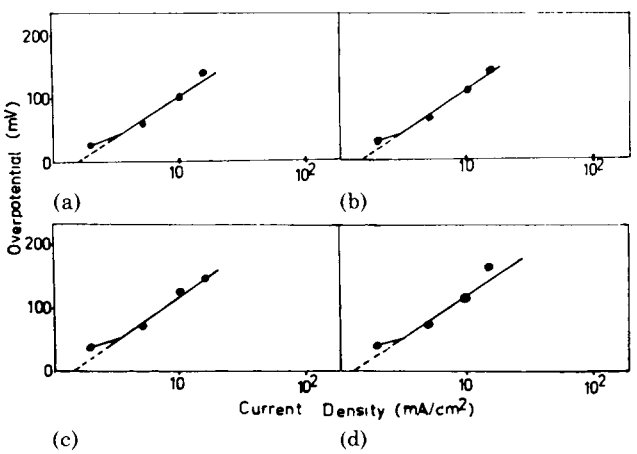



Fig. 22. Overpotential *vs* current density for copper deposition onto Cu(100) in acidic copper sulphate solution containing various concentrations of sulphanilamide: (a) pure solution, $b$ = 116.2 mV, $i_0$ = 1.5 mA $cm^{-2}$, (b) copper sulphate solution containing $10^{-11}$ mol $l^{-1}$ sulphanilamide, $b$ = 126.5 mV, $i_0$ = 1 5 mA $cm^{-2}$, (c) copper sulphate solution containing $10^{-9}$ mol $l^{-1}$ sulphanilamide, $b$ = 132 9 mV, $i_0$ = 1 4 mA $cm^{-2}$, (d) copper sulphate solution containing $10^{-6}$ mol $l^{-1}$ sulphanilamide, $b$ = 126.3 mV, $i_0$ = 1.35 mA $cm^{-2}$

when pyramidal deposits were obtained the overpotential was constant throughout the deposition time although the initial value was higher in the presence of sulphanilamide than it was for the pure solution. Under highly purified conditions the Tafel slope (Fig. 22) was found to be $120 \pm 5$ mV and the exchange current density was 1.5 mA $cm^{-2}$ for the steady value of the overpotential. The presence of sulphanilamide (up to $10^{-5}$ mol $l^{-1}$) did not change the Tafel slope ($130 \pm 5$ mV) and the $i_0$ value was 1.4 mA $cm^{-2}$ Plots of overpotential as a function of current density for various concentrations of sulphanilamide are given in Fig. 22.

## 4. Discussion

Several mechanisms have been proposed to explain the varying action of addition agents in the electrodeposition process; of these the surface adsorption theory and the complex ion [14] theory seem to be most pertinent in the present context. The observed $2RT/F$ values for the Tafel slopes in pure solution on the Cu(100) plane and on a polycrystalline surface are in accordance with

$$Cu^{2+} + e \xrightarrow{\text{slow}} Cu^{+}$$

$$Cu^{+} + e \xrightarrow{\text{fast}} Cu$$

as found by Mattson and Bockris [15] and Bockris and Kita [16]. The Tafel slope in the presence of low concentrations of sulphanilamide was found to be $130 \pm 5$ mV. This indicates that there is no change in the reaction path, *i.e.* that the first electron transfer is the rate-determining step

It is known [17] that sulphanilamide forms a complex (1:2) with copper(II) in acidic [18] copper sulphate solution. At low current densities the complex may be in the outer Helmholtz plane, decomplexation may then take place, causing the rate of deposition to slow down to some extent. However, at higher current densities the complex may be adsorbed at the electrode, leading to an increase in overpotential.

The change from layer growth to shortened layers and then to ridges at the current densities studied may be explained [15] as follows. The excess of sulphanilamide in each case obstructs a considerable number of the growth sites on the active surface and finally hinders growth so much that the formation of a nucleus for a new layer requires a smaller activation energy than further growth of the old layer. The old layer stops growing and instead a new layer starts to grow. Thus the result of increasing the concentration of sulphanilamide is always shortened layers. The truncation of square pyramids may be explained as follows. The complex may be specifically adsorbed on active sites on the Cu(100) face and also on the apexes of the pyramids and thus the vertical growth of the pyramid may be hindered, leading to truncated pyramids (Figs. 11 - 13, 17 and 18).

At higher concentrations (above $10^{-5}$ mol $l^{-1}$) of sulphanilamide the

complex may be precipitated at growth sites or at the interface region where it obstructs the incorporation of copper adions, causing an increase in overpotential and random nucleation. The random nucleation results in a polycrystalline deposit, and the Tafel relation no longer holds

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